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Visualization of Fruit Odor by Photoluminescence

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Abstract—Photoluminescence with visible emission spectrum was observed and visualized at the surface of certain fruits. This photoluminescence is associated with vapors of natural organic volatiles (odorants) emitted from the fruit surface. The photoluminescence spectra of various fruits (apple, pear, kiwi, and strawberry) were measured in vivo using a number of fluorometric methods. Fruit aging was found to be accompanied by modification of the photoluminescence spectrum shape and a noticeable increase in the photoluminescence intensity. Laser photoluminescence microscopy in vapors of fruit extracts and artificial compounds was used to assess the contribution of various substances to natural odor emission of fruits. The results of this study show that fluorometry of odors is a promising method for studying fruits and other objects.

Although it is well known that living systems produce a broad range of organic volatile compounds, the processes of gas exchange during natural emission of these compounds are insufficiently understood. Mixtures of gases and vapors of various chemical structure and broad concentration range are thought to be perceived as odors. Compounds responsible for specific odors are usually emitted as a component of a complex gas mixture containing other organic volatiles. Volatiles are usually emitted in excess by living systems; excessive amounts of volatile compounds represent the dynamic state of the system and can be used for its identification. Although odorants constitute a minor fraction of food, their analysis is of considerable interest, because it can be used for quality control. In addition, aromatic properties of food provide information about its geographic origin. Odors also affect the consumer value of products and demand for them. Therefore, odors are important criteria of product quality, and information about the product odor is of considerable economic significance. Monitoring of volatile emission from fruits and vegetables can provide crucial information about the optimum time of harvesting and optimum conditions of storage. Elucidation of odor emission mechanisms is of considerable practical importance. This information has a broad range of practical implications: from environmental monitoring and technological control in the industry to clinical diagnosis in medicine. In addition, odor identification can provide a methodological basis for studies of specific stages of biosynthetic processes and the molecular mechanisms of their regulation.

Conventional approaches to odor analysis are based on chemical methods of isolation (extraction and separation) and identification of volatile organic compounds (high-resolution gas–liquid chromatography in combination with mass-spectrometry and/or infrared spectroscopy) [1–6]. The target compounds are identified by comparing their spectra with reference spectra of authentic substances and/or standard samples. However, in none of the isolation methods is the odor of the resulting extract completely identical to the genuine odor. In adaptation, it usually takes a long time to analyze odor by these methods. It was reported on the basis of isolation methods that fruits produce a broad range of volatiles, which can be qualitatively determined as complex mixtures of more than 200 organic compounds [2–9]. However, as noted above, only a few of these compounds are responsible for the specific odor of fruits.

Nondestructive real-time detection of volatile organic compounds is a subject of considerable interest in various areas of science and technology. An electronic system sensitive to specific odors (electronic sniffer) has been recently developed by Nakamoto et al. [10]. The sensitive element of the system is an array of sensors. The sensor resistance is changed as a result of the adsorption of gas molecules and interaction with volatile odorants. This effect is used in this system to measure the total concentration of volatiles [11–13]. A new method based on proton-transfer-reaction mass-spectrometry was recently suggested for the real-time detection of trace amounts of gases [14, 15]. This nondestructive method was successfully applied to food quality control, environmental monitoring [16], and real-time detection of organic volatiles emitted from fruits during aging [17]. Taking certain berries as an example, it was shown in [17] that the dynamics of relative concentration changes of volatiles emitted from fruits can be confidently described in terms of time-dependent changes in contributions of well-known volatile compounds. According to molecular weights, these compounds can be arranged as the following ascending series: methanol (32), acetaldehyde (44),

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ethanol (46), acetone (58), acetic acid (60), methyl acetate (74), a mixture of ketones and aldehydes (86), ethyl acetate (88), and a mixture of esters (102, 116, 130, and 140). It was also shown in [17] that the aging of fruits is accompanied by an intense emission of organic gases (primarily, methanol and ethanol).

Because of high sensitivity, fluorometry has been widely used in recent years in biomedical research and practice, biochemistry, pharmacology, organic chemistry, and some other sciences as an analytical tool designed to identify chemical compounds and provide information about their structure. However, this approach has not been applied so far to the comprehensive analysis of odors.

The goal of this work was to obtain fluorometric images of in vivo fruit odor photoluminescence in visible spectral region, to study the effect of fruit aging (by periodic real-time detection of photoluminescence spectra near the surface of some fruits), and to determine the contribution of various organic compounds to natural emission of fruit odors (by laser photoluminescence microscopy in vapors of artificial volatile compounds or volatiles extracted from fruits).

MATERIALS AND METHODS

Fruits (apples, pears, kiwi, and strawberry) harvested in various geographical areas were obtained from a local market in Aveiro (Portugal). The fruits were stored for several weeks in individual open containers at room temperature in normal atmosphere. Pure reference organic compounds (artificial and extracted) were provided by the Department of Chemistry, University of Aveiro.

Photoluminescence spectra were measured at room temperature using a Renishaw Raman Image Microscope-2000 photoluminescence microscope (Great Britain) equipped with a two-dimensional CCD-detector (1 cm^{-1} resolution). Photoluminescence was excited at 632.8 nm by a He–Ne laser (Spectra Physics-127, United States) with an output power up to 25 mW. Photoluminescence was measured in unpolarized configuration using the back-scattering geometry of local photoluminescence excitation and detection at the interface region (size, 10–200 μm) located near the microscope focus. The excitation light power density ranged from 2 to 8×10^4 W/cm^2. The photoluminescence spectra were recorded within the range from the Stokes to the anti-Stokes shifts of ±3500 cm^{-1}.

To check if the recorded spectra were true photoluminescence features, the measurements were also performed using an argon-ion laser (Spectra Physics-2016, United States) (excitation wavelength, 514.5 nm; output power, up to 800 mW) and a double monochromator SPEX 1403 (United States) (spectral resolution, 4 cm^{-1}) equipped with a Hamamatsu PMT (Japan) photomultiplier detector. Photoluminescence measurements were performed with a 90° scattering geometry with the excitation laser beam parallel to the sample surface. The distance between the laser beam and sample surface was 2–5 mm. In addition, photoluminescence spectra were measured at different temperatures and in gas mixtures of various compositions. These measurements were performed using SPEX DM 3000 F and Jobin Yvon-SPEX Fluorolog-3 spectrofluorometers (United States). Photoluminescence in these spectrofluorometers was excited with 150-W and 450-W xenon arc lamps, respectively. The excitation wavelengths (±2 nm) were selected using appropriate monochromators and combinations of glass filters. The least-squares fit of the resulting spectra was obtained assuming a Gaussian shape of each band. Spectral components were calculated using the Microcal Origin-5 program (Microcal Software Inc., United States).

RESULTS AND DISCUSSION

For the first time, the photoluminescence of fruits was observed incidentally during laser micro-Raman spectroscopic measurements. The photoluminescence spectra were recorded within the spectral range from the anti-Stokes to Stokes shifts of ±3500 cm^{-1} (518–812 nm) upon excitation with a He–Ne laser at 632.8 nm. A typical spectrum of an intact apple is shown in Fig. 1a, curve *1*. The microscope focus (detection site) in this experiment was at a distance of 2 mm from the fruit surface and the focal area size was ≈20 μm. It is seen from Fig. 1a that the resulting photoluminescence spectrum contains a very strong Stokes peak at 684 nm and a relatively weak Stokes band or a shoulder at 710 nm (positions of spectral maxima correspond to Raman shifts of 1130 and 1900 cm^{-1} relative to the He–Ne laser excitation wavelength, respectively). We also tested if these bands can be caused by Raman scattering. To test this, the Stokes and anti-Stokes spectral regions were compared. No noticeable anti-Stokes spectral features were observed (Fig. 1a, curve *2*). Therefore, the Raman contribution to the Stokes region spectra shown in Fig. 1a, curve *1*, is negligible, and these spectra can be attributed to photoluminescence.

Epicarpium (subsurface area) of fruits is a complicated system composed of several layers coated with a thin protective outer membrane (cuticle). The cuticle regulates the gas content inside the fruit and gas exchange with the surrounding medium. Therefore, it is interesting to compare the photoluminescence spectrum recorded near the whole apple peel with similar spectrum recorded at the apple pulp surface (mesocarpium). The photoluminescence spectra of an apple recorded under otherwise identical conditions near the apple peel surface and near the pulp are shown in Fig. 1a (curves *1* and *3*, respectively). Note that the spectrum shown in curve *3* is magnified tenfold relative to the spectrum shown in curve *1*. A comparison between these curves shows that the photoluminescence spectrum shown in Fig. 1a (curve *1*) can be attrib-

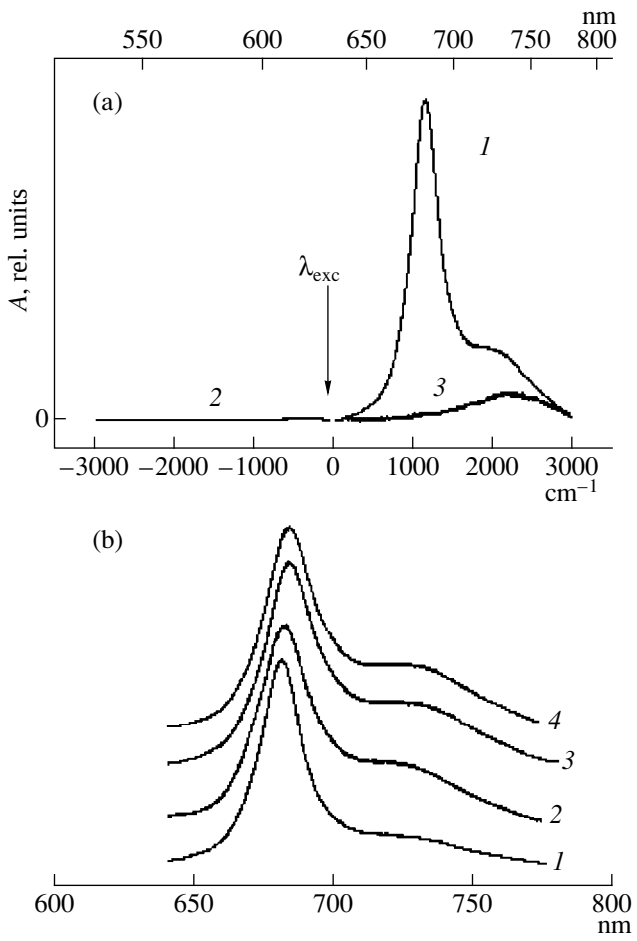

Fig. 1. Photoluminescence spectra of different fruits. (a) Typical spectrum of photoluminescence as measured near fruit (apple) surface (at a distance of 2 mm from the apple peel) in spectral region corresponding to: (*1*) Stokes and (*2*) anti-Stokes ranges of wavenumbers (±3500 cm^{-1}) (bottom abscissa) corresponding to the wavelength range 518–812 nm (top abscissa) relative to excitation at the wavelength of He–Ne laser λ_{exc} = 632.8 nm at excitation density of 4×10^4 W/cm^2; (*3*) measured near pulp surface of a piece of the same apple (tenfold magnification). (b) Normalized photoluminescence spectra of different fruits: (*1*) apple; (*2*) strawberry; (*3*) pear; (*4*) kiwi (λ_{exc} = 632.8 nm).

uted to specific processes occurring near the fruit peel surface.

All fruit species studied in this work (apples, pears, kiwi, and strawberry) were shown to emit photoluminescence within the spectral range of 640 to 800 nm. The normalized photoluminescence spectra of the fruits (excitation wavelength, 632.8 nm) are shown in Fig. 1b. Although the photoluminescence spectra of different fruit species are remarkably similar to each other, there is a certain difference in the spectral band shape and insignificant variability in positions of photoluminescence maximums at 680–685 nm.

Because fruit surface is rich in volatile compounds, it can be a source of fruit photoluminescence. Besides, chlorophyll may also contribute to this effect, because its luminescence spectrum falls within this range of wavelengths [18]. In addition, molecules of gases emitted into the surrounding atmosphere as a result of biochemical reactions in fruits may also contribute to photoluminescence. To elucidate the mechanism of photoluminescence generation in fruits, we studied the dependence of the photoluminescence spectra on the distance from the site of measurement to the fruit surface. The photoluminescence spectra recorded at different distances of the microscope focus location (from the site located at apple surface to the distance of 30 mm from the surface) are shown in Fig. 2a. Although the total intensity of photoluminescence declined with increasing distance, the shape of the spectrum remained virtually unchanged. The dependence of the maximum photoluminescence intensity on the distance from the fruit surface is shown in Fig. 2b. It is quite reasonable to suggest that the concentration of gas molecules emitted from fruit is maximal near the fruit surface and declines as the distance from the surface increases. According to the preliminary results of fruit photoluminescence measurements in a nitrogen atmosphere, neither chemical (photochemical) reactions in gases nor the resulting redistribution of gases near the fruit surface contribute noticeably to photoluminescence. Therefore, the photoluminescence yield dependence on the distance from the fruit surface suggests that it is the natural gas atmosphere near the fruit surface that is the main source of the photoluminescence observed in our experiments. Free vapor of chlorophyll-like compounds has not been yet detected in natural systems, whereas the shape of the photoluminescence spectra near fruit surface is virtually the same as the shape of the spectra recorded sufficiently far from the surface. Therefore, it is reasonable to suggest that photoluminescence is due to volatile odorants emitted into the surrounding atmosphere from the fruit surface. Our findings that the distribution of photoluminescence induced by the laser beam parallel to the fruit surface coincides with the photoluminescence distribution with perpendicular orientation of the excitation laser beam direction relative fruit surface can also be regarded as additional evidence of the mechanism of photoluminescence based on fruit gas emission. It should also be noted that changes in the excitation power density caused by the He–Ne laser beam focusing variation from 10 to 200 μm and excitation power variation from 2.5 to 25 mW had no effect on the positions of photoluminescence peaks but were accompanied by corresponding changes in the photoluminescence intensity (Fig. 3a).

To modify the natural conditions of gas emission from fruit surface, an apple was cut into pieces and the peel of one piece was pressed against the surface of a circular quartz plate. Photoluminescence was excited and detected through the quartz plate. The pressing force was varied using a special cylindrical cramp (Fig. 3b). Before pressing (i.e., under conditions of a

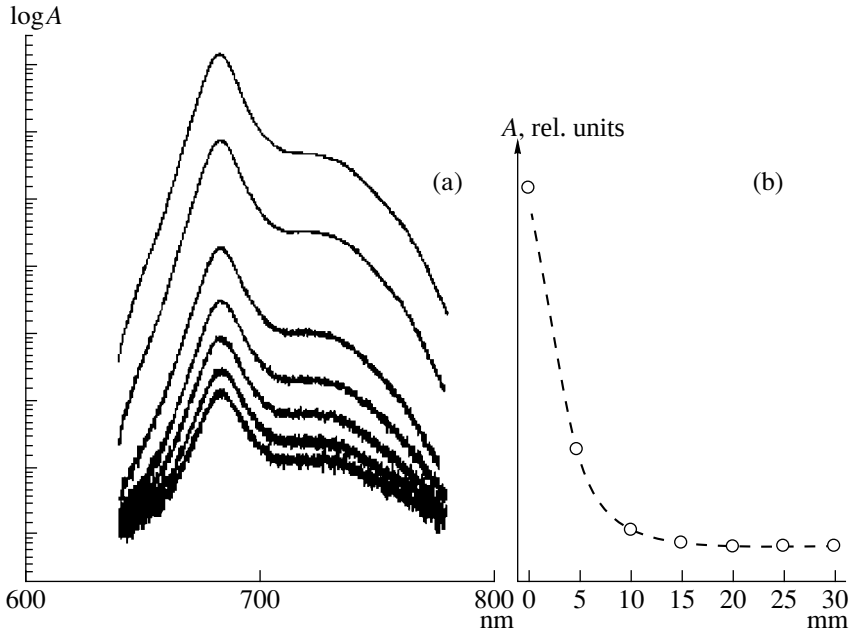

Fig. 2. Dependence of photoluminescence intensity on the distance. (a) Dependence of photoluminescence intensity logarithm on the distance between fruit (apple) surface and site of spectral measurement (from top to bottom): from spectrum at sample surface to spectrum recorded at a distance of 30 mm; the distance was varied with a step of 5 mm; focal zone size, ≈20 μm; excitation wavelength λ_{exc} = 632.8 nm (spectra are shown without vertical shift). (b) Dependence of photoluminescence intensity maximum on distance.

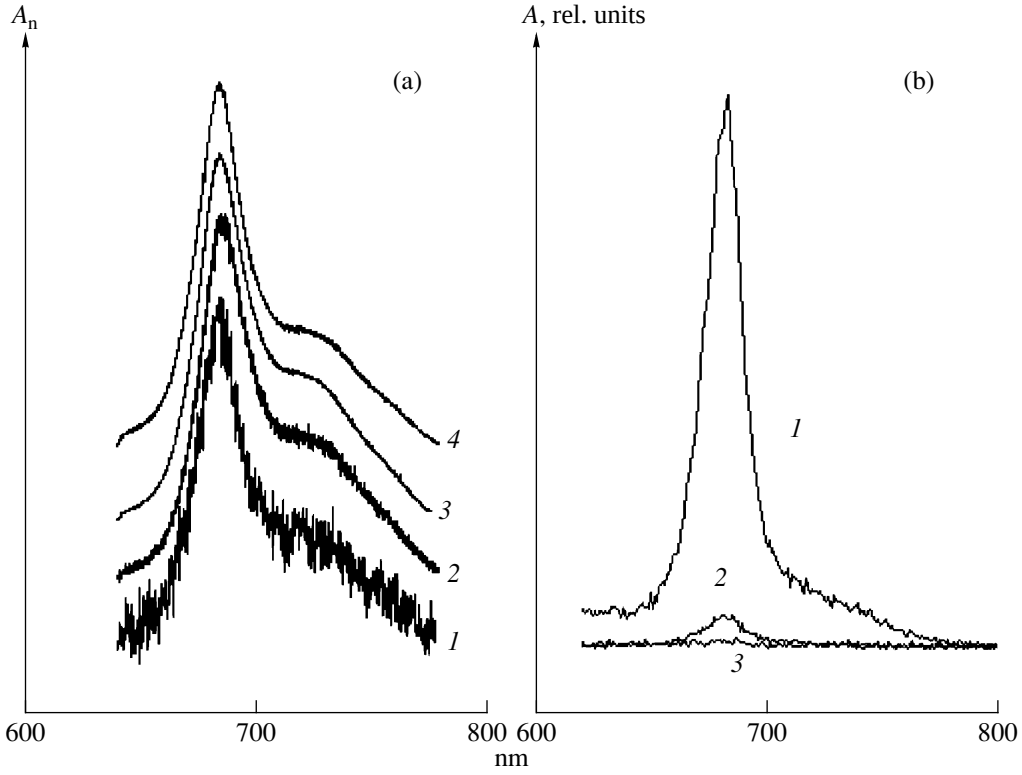

Fig. 3. Dependence of photoluminescence intensity on experimental conditions. (a) Photoluminescence spectra recorded near a fruit (apple) sample at different levels of excitation power density (He–Ne laser). Laser beam was focused to the spot size of 10 and 200 μm. Excitation power was 2.5 and 25 mW: (*1*) 10 μm, 2.5 mW; (*2*) 200 μm, 2.5 mW; (*3*) 200 μm, 25 mW; (*4*) 10 μm, 25 mW. (b) Photoluminescence spectra of an apple sample pressed against the surface of transparent quartz plate (apple peel is oriented toward the plate): (*1*) before pressing; (*2*) pressing up to disappearance of air bubbles; (*3*) maximum-force pressing until juice is pressed out (photoluminescence was excited at λ_{exc} = 600 nm using a xenon lamp).

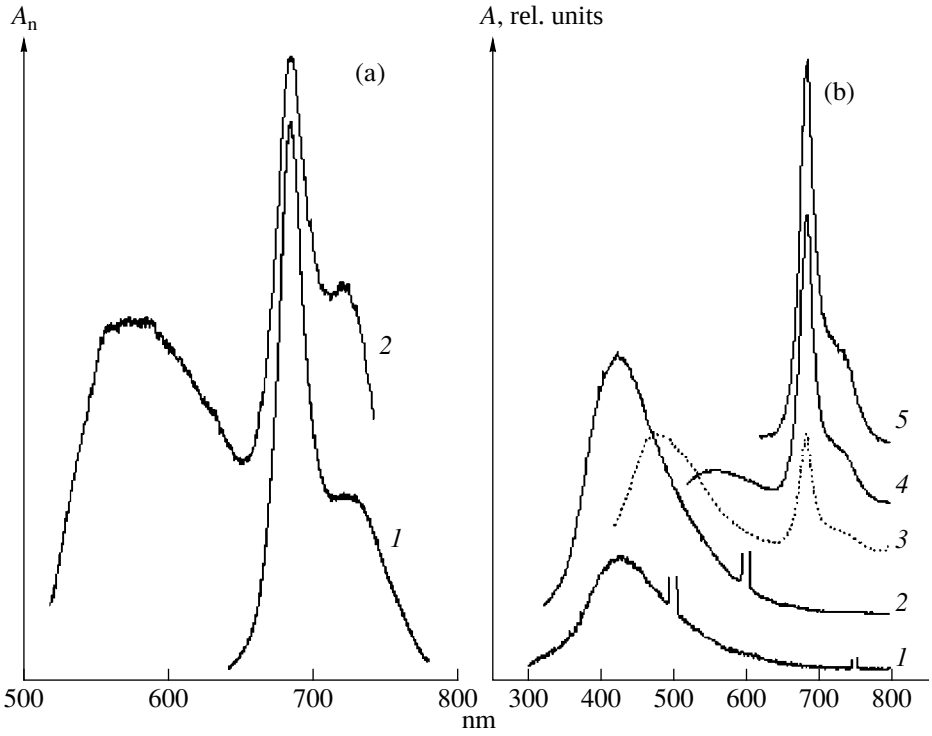

Fig. 4. Photoluminescence spectra of a fruit (kiwi) at various excitation wavelength: (a) laser excitation: (*1*) 632.8 nm; (*2*) 514.5 nm; (b) excitation with xenon lamp: (*1*) 250 nm; (*2*) 300 nm; (*3*) 400 nm; (*4*) 500 nm; and (*5*) 600 nm.

slight touch between the fruit peel and the plate), the photoluminescence was sufficiently intense (Fig. 3b, curve *1*). An increase in pressure caused an irreversibly decreased photoluminescence intensity (Fig. 3b, curves *2* and *3*). Thus, under conditions of restricted free gas exchange, the photoluminescence intensity near the fruit surface is negligible. However, in addition to gas exchange inhibition, apple pressing against a glass plate is also accompanied by uncontrolled destruction of the sample structure.

To study the specific features of photoluminescence, the excitation wavelength (λ_{exc}) was varied within the range from 250 to 650 nm (see *Materials and Methods*). Typical spectra of kiwi fruit photoluminescence excited by laser (514.5 and 632.8 nm) and monochromatic light of a xenon lamp are shown in Figs. 4a and 4b, respectively. Within the spectral range 650–800 nm (Fig. 4a, curves *1* and *2*, and Fig. 4b, curves *3–5*), the main peak at 684 nm and minor spectral features at 700–730 nm were observed upon excitation at different wavelengths. Therefore, these spectral features are due to photoluminescence. This interpretation is also consistent with the results of measurements in the Stokes and anti-Stokes spectral ranges discussed above (Fig. 1a). As the excitation wavelength decreased to 250 nm, there was a decrease in the photoluminescence intensity at 650–800 nm, whereas a broad high-energy zone was dominant in the spectral region near 420 nm (Fig. 4b, curves *1* and *2*). This zone of intense luminescence was observed at λ_{exc} = 250 and 300 nm and various excitation energies. Therefore, it can also be attributed to photoluminescence. As the excitation wavelength increased, the intensity of the high-frequency zone declined, and its spectral maximum was shifted from 420 nm up to 570 nm (Fig. 4b, curves *2–4*). In our opinion, this shift may result from the photoexcitation of a mixture of different gases emitted from fruits. The photoluminescence spectra of the fruit species studied in this work arbitrarily fall into two groups: (*1*) strong peaks at 350–430 and 680–685 nm; and (*2*) relatively weak peaks at 470–570 and 700–730 nm.

Since the spectrum of photoluminescence is in the visible region, the distribution of photoluminescent gases near the fruit surface can be photographed. The photoluminescence of fruits was imaged using color photography and near-UV excitation (150-W medium-pressure mercury lamp; UV optical filters). Photoluminescence was detected in a dark room using a Pentax Espio-160 photographic camera equipped with UV filters. Photographic images of an apple and a kiwi are shown in Fig. 5 (left and right, respectively). The images were obtained as a result of analog-to-digit conversion and decomposition into red, green, and blue components of color image (red, green, and blue components are shown in Fig. 5 from top to bottom). It is seen from Fig. 5 that blue and green components of the resulting image are dominant. These components correspond to the photoluminescence bands at 470–570 nm (Fig. 4b, curves *2–4*). Therefore, it is beyond doubt that odor can be visualized. The images shown in Fig. 5 rep-

resent the photoluminescence intensity distribution near fruit surface as a glowing diffuse halo, the intensity of the halo decreasing as the distance to the fruit surface increases. This trend is consistent with the photoluminescence intensity dependence on the distance from the fruit surface (Fig. 2).

The possible contribution of different organic compounds to natural emission of fruit odor was studied using laser photoluminescence microscopy in the vapors of artificial organic volatiles and natural fruit extracts (excitation wavelength of He–Ne laser, 632.8 nm). A kit of 22 liquid (under normal conditions) organic compounds was used (table). These compounds were chosen, because they are dominant components of the complicated mixture of organic volatiles identified in fruits [6, 7, 9, 17].

As expected, we did not observe any noticeable photoluminescence of free vapors of liquid compounds in open containers at room temperature. However, a modified version of the method of measurement allowed detection of the photoluminescence of these compounds. A few droplets of the compound of interest were applied to a piece of filter paper at room temperature. The filter paper was placed in a closed glass or fluoroplastic container with a small gas outlet (diameter, 0.5 mm; length, 1 mm). The escaping vapor molecules were analyzed using a photoluminescence microscope focused accurate to 10–20 μm at the center of the hole (nozzle). The results of the measurements of methanol photoluminescence in the liquid phase and the gas phase (vapor at the outlet nozzle) are shown in Fig. 6. The spectrum of liquid methanol (microscope focus was in liquid) is shown in Fig. 6a. This spectrum is characterized by narrow Raman modes, whereas the spectrum of methanol vapor (Fig. 6b) contains a dominant strong photoluminescence band at 678 nm. The photoluminescence spectrum of methanol vapor was approximated by a sum of four Gaussian components (Fig. 6b).

The photoluminescence of vapors of other compounds was also observed at the nozzle outlet. Normalized photoluminescence spectra of some compounds are shown in Fig. 7. It should be noted that different compounds have different intensities of photoluminescence. At room temperature, the most intense photoluminescence was emitted by vapors of methanol, ethanol, and ethyl acetate. The results of spectral analysis of the 22 compounds tested in this work are given in the table (spectra were analyzed within the wavelength range from 640 to 800 nm). Within this spectral range, the photoluminescence zones of both individual volatiles and fruits at 670–685 nm are close to each other. It was not surprising that we failed to fit the fruit photoluminescence spectra by combinations of spectra of several individual compounds, because the number of compounds actually contributing to natural fruit odor is seemingly much larger than the number of compounds tested in this work. Therefore, fruit photoluminescence is a more complex superposition of the spectral contributions of individual compounds. Photoluminescence intensity in model gas systems was significantly lower than fruit photoluminescence intensity. This can be explained by either an excessive total concentration of volatiles in fruits or different physical conditions of emission from fruit surface and evaporation of model compounds. In addition, the relative contribution of each individual compound to fruit photoluminescence is not necessarily equal to the relative contribution of this compound in a model system.

The results of our study provide a new insight into the mechanisms of gas exchange at the fruit surface. The fruit surface coating (cuticle) is a specific lipid–cellulose membrane isolating from the surrounding medium. The cuticular membrane consists of two morphological components: the cuticle itself (amorphous pectin–cellulose matrix impregnated with lipid compounds) and structurized surface wax coating [19–22]. According to microscopic examination [19, 20], the fruit cuticle is a laminar structure composed of loosely packed layers. These layers are parallel to the fruit surface and separated from each other by lacunas (cavities of 0.001–1 μm in size). Some lacunas are filled with cellulose-like substances, whereas other lacunas are

Photoluminescence maximums in vapors of some volatile compounds

Compound	Maximum, nm			
	1	2	3	4
Methanol	653	678	703.4	756.6
Ethanol		679.3	693.5	746
Ethyl acetate		679	692	750.7
Ethyl caprylate		678	690	749.6
Ethyl caprylate		677.5	689	744
Ethyl caprylate		676.8	686.7	734.6
Acetaldehyde	651.3	679	696.2	744.7
Acetone		675.9	702	
Acetic acid	663	678	712.8	757.6
Methyl acetate	648	676.9	696	752
Octanol		676.8	687.7	749.2
Hexanol		677.8	690.3	751.4
Hexanal		677.6	689	752.3
Methyl butanol		677.7	689	738.7
Phenyl ethanol		677.6	689.6	742.2
Dimethylacetamide		676	689	742.3
Limonene		677.4	705.7	723
Geraniol		678	690	747.7
t-t-Farnesol		678.4	692	749.4
Nerol		678.4	694.5	755
Citral		676.3	703.8	723.7
Linalool		676.6	689.3	

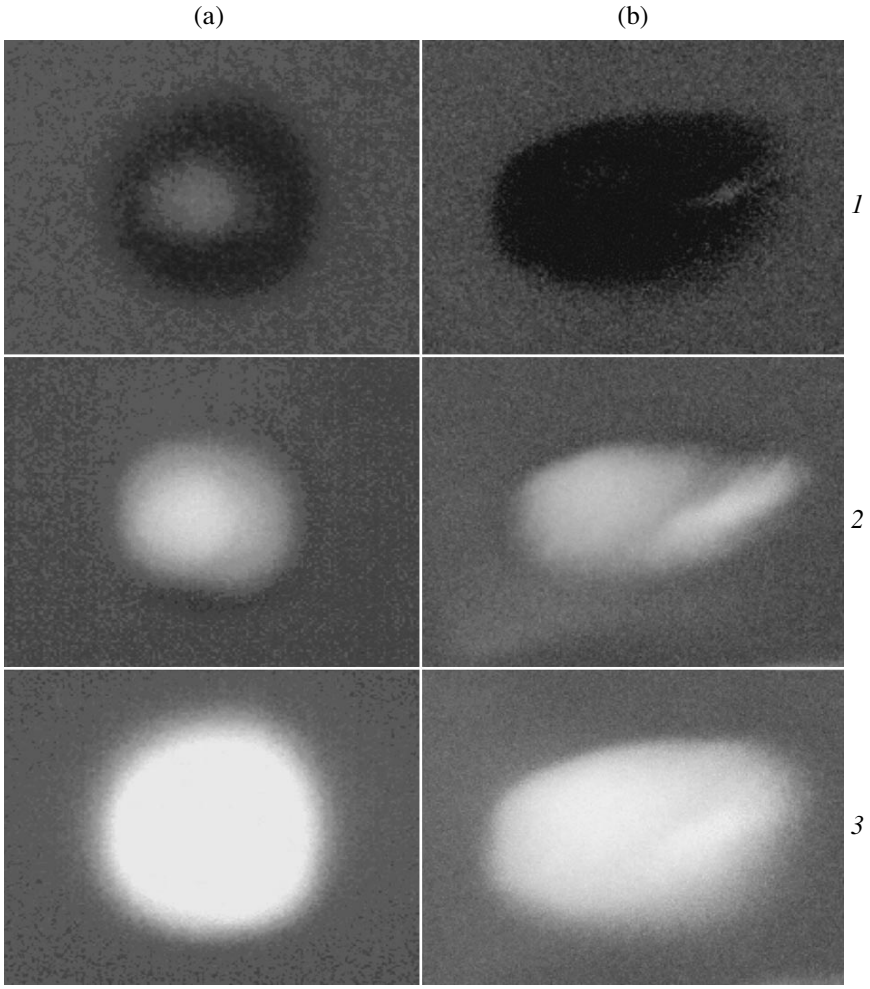

Fig. 5. Photoluminescence visualization near fruit surface: (a) apple; (b) kiwi. Photographs were taken using near-UV excitation (150-W medium-pressure mercury lamp and UV optical filters). Photoluminescence was detected using a common photographic camera equipped with a UV filter. Photographic images were obtained as a result of analog-to-digit conversion and decomposition into (*1*) red, (*2*) green, and (*3*) blue components of color image. The images represent photoluminescence intensity distribution near the fruit surface as glowing diffuse halo, the intensity of the halo decreasing as the distance to the fruit surface increases.

empty. Empty lacunas may have a substantial effect on the gas exchange, because their surface is able to adsorb volatile compounds emitted by fruits, thereby causing the accumulation of volatiles and increasing their concentration near the fruit surface. Gas exchange inside fruits can be described by diffusion (Devault effect) using such physical parameters as porosity (ratio of intracellular space volume to the total fruit volume), surface area to volume ratio, pore shape, and size [23]. An important feature of gas exchange in fruits is that the cuticular membrane is the major contributor to total diffusion resistance, whereas the bulk fruit pulp does not prevent the free diffusion of gases [24]. However, the processes of gas diffusion through subsurface tissues of fruits remain insufficiently understood. The physical properties of the cuticle as a diffusion membrane were discussed in [21, 22, 25] on the basis of a selective diffusion model suggested to explain the selective permeability of fruit surface to different gases (oxygen and carbon dioxide).

Neither properties nor mobility of gases during diffusion from the fruit surface have been studied so far. In this work, we observed photoluminescence of both fruit surface and gases of certain model compounds. However, no photoluminescence was observed in free vapors of these compounds. To excite photoluminescence in gases, vapors of model compounds were passed through a nozzle. It was found that this is a necessary condition of photoluminescence detection. Therefore, it is conceivable that directed movement of gas molecules through a nozzle is somewhat similar to natural processes of emission from the fruit surface.

Diffusion efficiency depends on the partial pressure gradient across the diffusion membrane and the physical properties of the membrane (Fick's law). The partial pressure of certain gases (e.g., oxygen and carbon diox-

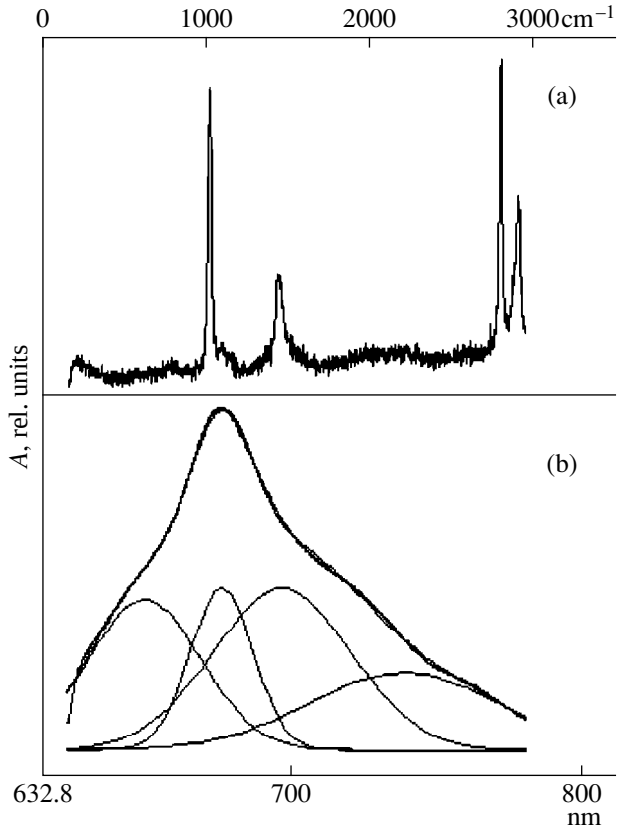

Fig. 6. Photoluminescence spectra of methanol in liquid and gaseous phases; (a) liquid phase spectrum (under otherwise invariable conditions, the focal point of microscope was shifted from vapors to liquid); (b) gaseous phase spectrum (spectral approximation).

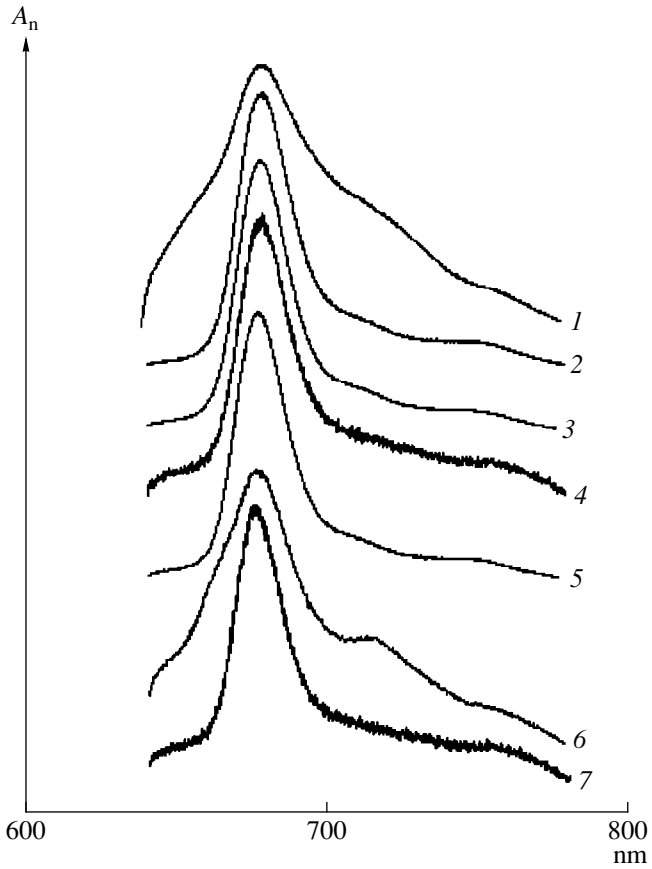

Fig. 7. Photoluminescence spectra of vapors of some compounds: (*1*) methanol; (*2*) ethanol; (*3*) ethyl acetate; (*4*) acetaldehyde; (*5*) ethyl caprylate; (*6*) acetate; (*7*) methyl acetate.

ide) both inside and outside fruits is significantly above the background level. Because relative concentrations of these gases in air are sufficiently high, a diffusion model can be used to describe their behavior. According to Fick's law, the efficiency of emission of volatile compounds through the cuticular membrane into the surrounding atmosphere should be significantly increased, because concentrations of volatiles in the atmosphere are negligible. Therefore, it may be suggested that the outlet gas movement is similar to its escape from cuticular pores to surface air layers.

We also studied the mechanisms of fruit photoluminescence. It is presently uncertain why the energy range of photoluminescence of different fruit species and organic volatile compounds is relatively narrow. In addition, the excitation energy in our experiments ranged from 1.9 to 4.9 eV. However, this range is far below the single-photon excitation energy threshold of the volatile molecules tested. For example, the lowest excited electronic level of the methanol molecule is above 6 eV [26]. Thus, if photoluminescence is not due to the transition of molecules to excited electronic states, it is reasonable to suggest that various vibronic states may contribute to photoluminescence generation. It is possible that the photoluminescence observed in our experiments is due to vibrational mobility of functional groups of certain volatile compounds.

A preliminary experimental study of natural aging of fruits is an example of the practical application of photoluminescence of fruits. Initially, each sample was placed in an individual open container and kept there at room temperature in natural atmosphere. These containers also prevented fruits from mechanical injury. The photoluminescence spectra were measured under identical experimental conditions, the same microscope focus distance (2 mm above the fruit surface), and equal levels of photoexcitation from the He–Ne laser. The results of changes in the photoluminescence parameters of two apple samples subjected to one-month-long aging are shown in Fig. 8. It follows from Fig. 8 that aging was accompanied by modification of spectral shape and a significant (approximately four-fold) increase in the photoluminescence intensity. It is interesting to note that no visible changes in the state of the apples were observed during one month of aging. The photoluminescence changes observed in these

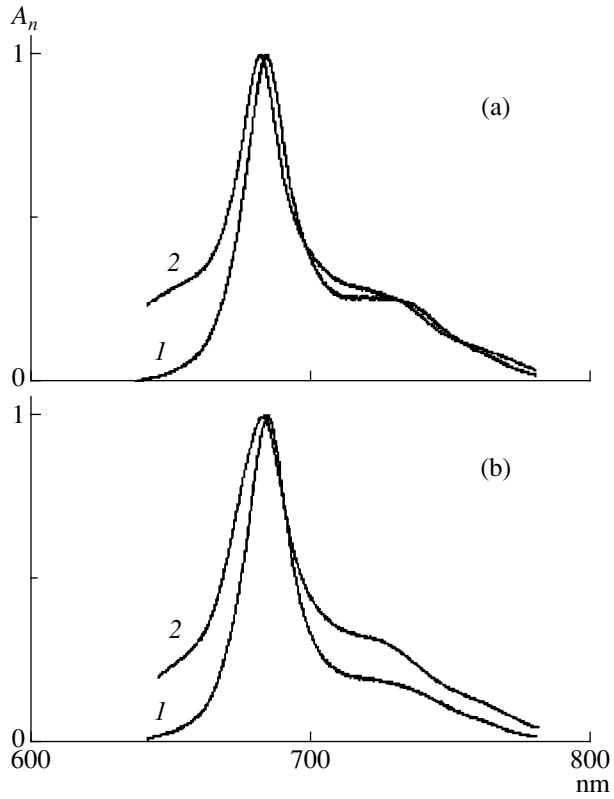

Fig. 8. Effect of apple aging for one month: (*1*) initial spectra of photoluminescence; (*2*) photoluminescence spectra recorded after one month of storage in open containers in laboratory under natural atmosphere. Photoluminescence spectra were normalized. Apple cultivars: (a) Star King (measured November–December 1997); (b) Golden (measured February–March 1999).

experiments can be primarily attributed to a possible increase in the diversity of gases emitted by fruits during aging. These processes are obviously associated with biochemical reactions in fruits during so-called climacteric and postclimacteric periods [25]. A comparison of the photoluminescence spectra shown in Fig. 8 with spectra of gases of individual compounds (Fig. 7) suggests that aging-related spectral changes are due to an increase in the relative concentration of dominant volatiles (methanol, ethanol, ethyl acetate, ethyl caprylate, acetic acid, etc.). However, more profound comparative studies of chemical processes in fruits exposed to various environmental conditions are required to provide a more substantiated insight into the mechanisms of fruit aging. In conclusion, it should be emphasized that the results of this work demonstrate that photoluminescence spectroscopy provides a promising approach to studies of biochemical changes in fruits.

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